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Collision-induced neutral loss reactions of molecular dications

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Collision-induced neutral loss reactions are observed to be a major product channel for reactions of CF_3^{2+}, SF_4^{2+}, SF_3^{2+} and SF_2^{2+} with the rare gases at 49 eV laboratory collision energy. This reactivity, which involves the formation of doubly charged molecular daughter ions, differs markedly from that observed for other molecular dications. The doubly charged product ion yield is largest for systems in which charge transfer does not compete effectively with the collision-induced process.

1. Introduction

Studies of gas-phase molecular dications have principally focused on the properties of the isolated species [1–8]. However, there is increasing interest in the bimolecular reactions of gas-phase molecular dications [9–14]. Recent studies of the collisional reactivity of molecular dications have concentrated on the interactions of commonly produced dications (e.g. N_2^{2+}, CO^{2+}, CO_2^{2+}, COS^{2+}) with the rare gases (Rg). These studies show a reactivity dominated by competition between charge-transfer (CT) reactions

$$AB^{2+} + Rg \rightarrow AB^{+} + Rg^{+}, \quad (1)$$

and collision-induced charge-separation (CICS) reactions,

$$AB^{2+} + Rg \rightarrow A^{+} + B^{+} + Rg. \quad (2)$$

In the intermediate collision energy regime, covering collision energies of approximately 0.1–200 eV, experiments show that charge transfer dominates the reactivity, although CICS is important when the CT channels are not energetically accessible [11–16].

In order to widen the scope of the available experimental information concerning dication bimolecular reactivity, we recently initiated a series of studies of the collisional reactivity of larger molecular dications. For several of these larger perfluorinated dications we observe an unusual collisional process, collision-induced neutral loss (CINL), as a major channel. This CINL reaction,

$$XF_n^{2+} + Rg \rightarrow XF_{n-1}^{2+} + F + Rg, \quad (3)$$

results in the formation of a stable *molecular* dication as a reaction product. To date, experiments have shown that the collisional chemistry of molecular dications is dominated by CT and CICS, and reports of bimolecular neutral loss reactions are scarce [9–14]. However, the mechanism of bimolecular reactions involving the loss of neutral species from molecular dications to form *atomic* dications has been investigated by translational energy spectroscopy at 5 keV collision energy [17]. This study concluded that two reaction mechanisms contributed to the atomic dication yield, one pathway involving dication electronic excitation and the second perhaps involving a curve crossing. The above study also reported the loss of neutral H atoms from CH_3I^{2+} in the 5 keV collisions, but this channel was not investigated in any detail [17].

In this Letter, we report that CINL reactions are an important decay channel, not a minor pathway, for larger fluorinated dications at collision energies

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below 100 eV. Given the usual high propensity for the Coulomb repulsion pathway in molecular dications, this result is surprising and gives important information about the potential energy surfaces and structures of this class of dications. We describe the collisionally induced neutral loss reactions observed following collisions of CF_3^{2+}, SF_4^{2+}, SF_3^{2+} and SF_2^{2+} with the rare gases, and briefly discuss possible explanations for their occurrence.

2. Experimental description

A detailed description of the experimental apparatus employed to study the reactions of molecular dications has appeared in the literature [14], and only a brief overview is presented here. Dications are generated in an ion source by the interaction of a beam of ≈ 150 eV electrons with a continuous beam of neutral precursor. The precursors CF_4 and SF_6 were used for the generation of CF_3^{2+} and SF_n^{2+} species. The ion source is held at a specific voltage which determines the kinetic energy of the dication beam. Ions are extracted from the source and focused into a quadrupole mass spectrometer (QMS). The QMS rejects all the ions formed in the source except the dication of interest. This ion beam is then focused into a collision region where it interacts with a pulsed jet of rare gas collision partner. The number density of the rare gas atoms is carefully controlled to ensure that single-collision conditions exist in this interaction region. Except where noted, all the results reported here are for collisions at a laboratory kinetic energy of 49 eV.

Both the ion products from the collisions and unreacted dications are extracted from the collision zone into the source region of a time-of-flight mass spectrometer which is used to detect and identify the ions. A deflector arrangement in the drift tube of the time-of-flight mass spectrometer is used to compensate for the lateral velocity of the precursor ion beam and allow the ions to reach a multichannel plate detector. The ion collection efficiency of this experimental arrangement has been described before in the literature [14,15]. The design of the apparatus is such that the fast product ions derived from the molecular dication are detected with high efficiency [15].

Product ion mass spectra are recorded before and after the rare gas jet is pulsed. The spectrum recorded before the rare gas jet pulse is a background spectrum that contains signals from both unimolecular decay processes and collisions with background gases. These background signals, which are very small, are subtracted from the spectra recorded after interaction with the rare gas jet to obtain the product ion signals resulting solely from the collision. The net product ion signals are corrected for the small mass discrimination effects introduced by the deflectors to obtain the product ion yields for a given reacting system. Estimates of the errors in these yields are determined from the standard deviation of a series of measurements.

3. Results

Fig. 1 shows product ion mass spectra recorded following collisions of CF_3^{2+} with Xe and SF_4^{2+} with Ne. The occurrence of the collision-induced neutral loss reactions is clearly illustrated by the distinct CF_2^{2+} signal in the CF_3^{2+}/Xe system (fig. 1a) and the SF_3^{2+} and SF_2^{2+} ions observed following collisions of SF_4^{2+} with Ne (fig. 1b). Note that the CINL reactions of SF_4^{2+} produce two dicationic products: SF_3^{2+} and SF_2^{2+}, as is clearly shown in fig. 1b. Similar CINL reactions are observed following collisions of SF_3^{2+} and SF_2^{2+} with the rare gases. All the CINL reactions observed to date are listed in table 1. In each of the systems which react by CINL (table 1), a small signal due to CICS is also observed in addition to that from neutral loss reactions.

Fig. 2 shows the CF_2^{2+} ion yield of the collision-induced neutral loss reaction of CF_3^{2+} (forming $CF_2^{2+} + F$) as the rare gas collision partner is varied from He to Xe. Fig. 2 shows a marked decrease in the ion yield of the collision-induced process as the rare gas collision partner is changed from He to Xe, although an initial increase in the yield is observed on changing from He to Ne. Note that the data presented in fig. 2 are all at the same laboratory frame kinetic energy. However, the decrease in the CINL yield displayed in fig. 2 is not a result of the greater center of mass kinetic energy in the heavier reduced mass systems. The increase in the center of mass kinetic energy as the collision partner is changed to heavier rare gas atoms is expected to result in an in-

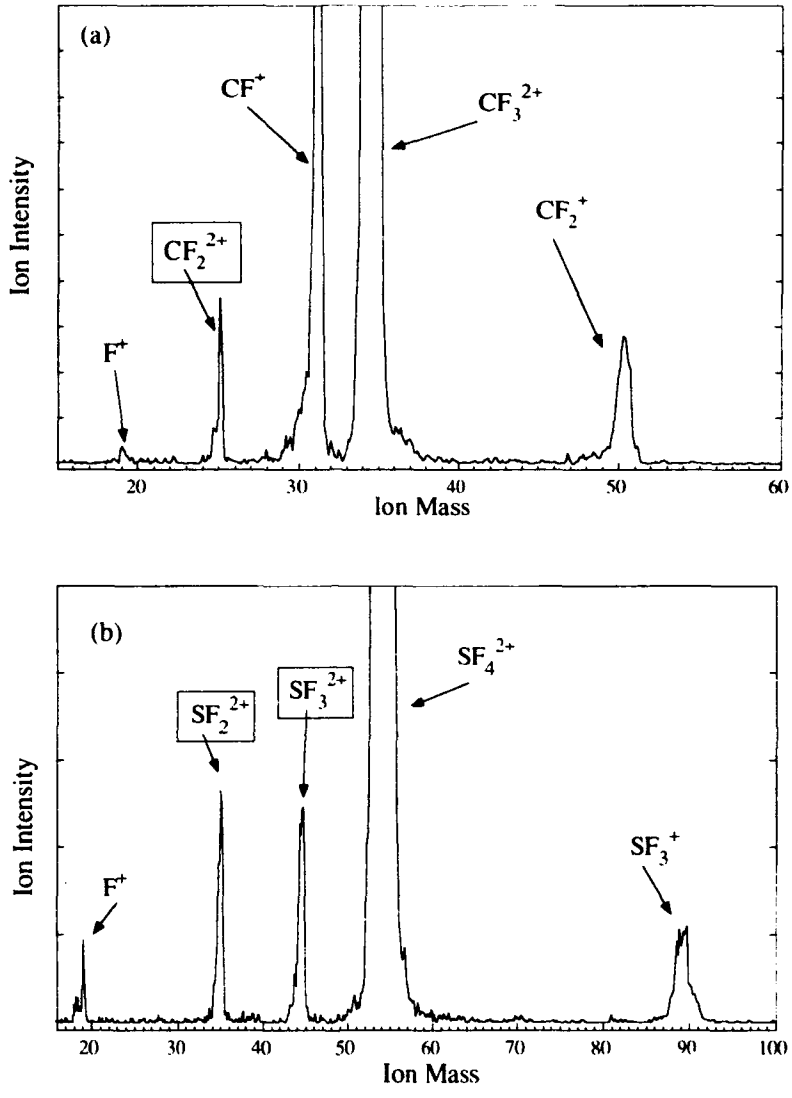

Fig. 1. Product ion mass spectra recorded following collisions, at 49 eV laboratory kinetic energy, of (a) CF_3^{2+} with Xe and (b) SF_4^{2+} with Ne.

crease, not the observed decrease, in the yield of the collision-induced processes in the collision energy regime below 100 eV [18]. A similar general decrease in the ion yield of the neutral loss reaction, on moving to heavier collision partners, is observed in the SF_n^{2+}/Rg systems. In fact, the CINL reactions of SF_4^{2+} and SF_2^{2+} become too small to observe with the heavier rare gases (table 1).

For the SF_4^{2+}/He system no CINL reaction is observed at 49 eV laboratory collision energy. However, on raising the laboratory collision energy to 160 eV, approximately 30% of the ionic products are due to the neutral loss process. This observation suggests that the neutral loss process has an activation energy. It appears that this activation energy cannot be supplied in collisions with the light He atom at $E_{lab}=49$ eV because of the low center of mass kinetic energy of this system. Raising the laboratory collision energy raises the energy transferred in the collision, and allows the system to undergo neutral loss.

Table 1
Relative yield of the observed collision-induced neutral loss reactions at 49 eV laboratory collision energy

Reactant dication	CINL yield (%) [a]					Product dication
	He	Ne	Ar	Kr	Xe	
CF_3^{2+}	95	86	26	5	2	CF_2^{2+}
SF_4^{2+}	< 1 [b]	59	18	2	< 1	SF_3^{2+}, SF_2^{2+}
SF_3^{2+}	95	97	41	20	12	SF_2^{2+}
SF_2^{2+}	25	25	< 1	< 1	< 1	SF^{2+}

[a] The relative CINL yield is expressed as a percentage of the total product ion yield. Uncertainties in these values are approximately ± 10%.

[b] CINL reactions are observed for the He/SF_4^{2+} system at higher collision energy. See text for details. The numbers are the sum of the two channels.

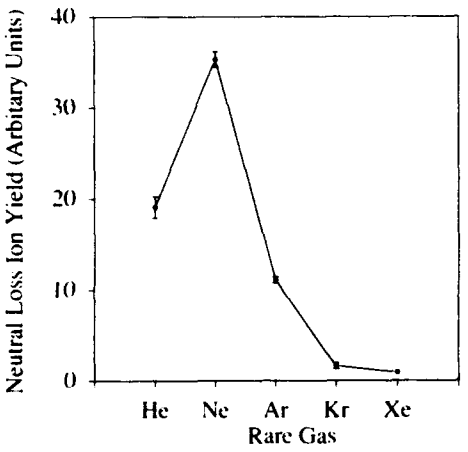

Fig. 2. Plot of the CF_3^{2+} neutral loss ion yield as a function of rare gas collision partner. All the experiments were performed at 49 eV laboratory collision energy.

4. Discussion

There are several questions that arise from the above experimental results. How can the large percentage yield of the CINL process with He and Ne and the decrease in this yield as the rare gas collision partner changes from Ne to Xe be understood? What characteristic of the CF_3^{2+} and SF_n^{2+} dications allows for the effective competition between neutral loss reactions and charge separation reactions following collisional excitation?

The decrease in the importance of the CINL reaction in collisions with the heavier rare gases (fig. 2) is a result of the competition between CINL and charge-transfer reactions. Previous studies of dication reactions, at intermediate collision energy, show that charge-transfer reactions dominate the reactivity with the rare gases when these are exothermic paths [12–16]. We find that this is also the case for the dications studied in the current experiments. However, for the majority of molecular dications, the charge-transfer channels with He and Ne are intrinsically endothermic. For an endothermic charge-transfer reaction in the intermediate collision energy regime, no curve crossing mechanism exists between the reactant and product potential energy surfaces and hence endothermic charge-transfer channels are not favored [14–16]. The reactivity of the CF_3^{2+} and SF_n^{2+} dications studied in this work conforms to the above model; with He and Ne little charge-transfer reactivity is observed, and every collisional excitation event can result in a collision-induced process (CINL or CICS). However, collisions with the heavier rare gases do not necessarily result in a collision-induced reaction (CINL or CICS) since CT can occur with a significant probability. We can therefore account for the decrease in the yield of the CINL reaction with the heavier rare gases as due to the increased propensity for charge transfer in these systems, which masks the effects of dication collisional excitation.

The increase in the CINL yield on moving from He to Ne (fig. 2) is most likely due to the increased center of mass kinetic energy available for dication excitation, as well as the larger target atom size. With Ne, the charge-transfer channel is not yet energetically accessible and hence no competition between charge transfer and CINL is present. Hence, both the

increase in the center of mass kinetic energy and the collisional cross section result in an increase in the CINL yield.

To understand why collisional excitation of some dications results in both CINL and CICS (e.g. CF_3^{2+}) whereas other dications (e.g. CO^{2+} or OCS^{2+}) only undergo CICS [11,14,15], we consider the mechanism for the CINL reaction. One can picture a general mechanism where the competing CINL and the CICS processes are not directly coupled, but where two different non-interacting reaction pathways correspond to the two collision-induced processes. Thus, energy transfer in the collision allows the dication to pass over a barrier to CINL products, or over another barrier to CICS products. The barrier to CINL could correspond to the vibrational excitation required to break an X–F bond or to the energy required to achieve a promotion to a dissociative electronic state. Following the conventional arguments for collision-induced dissociation [18], the occurrence of a CINL reaction could indicate a weak XF_{n-1}^{2+}–F bond (low barrier), which is easily broken following dication excitation in the collision. Such a model of the CINL reaction is rather simplistic and undoubtedly does not incorporate the full multidimensionality of the polyatomic dication potential energy surface. However, if this simple bond strength argument is essentially correct, one could picture these larger dications as being made up of a strongly bound dication core (e.g. CF_2^{2+} or SF_2^{2+}) bonded weakly to one or more fluorine atoms.

Fig. 3 illustrates an alternative CINL reaction

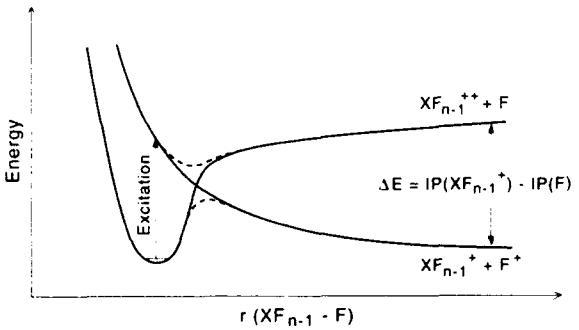

Fig. 3. Schematic potential energy surfaces for a charge-transfer mechanism of the collision-induced neutral loss reaction. See text for details.

mechanism where the neutral loss reaction occurs due to a charge-transfer reaction in the CICS exit channel. The energy transfer in the collision accesses initially the charge-separating state, and there is an appreciable probability of a curve crossing to the neutral loss potential energy surface as the ions separate. The character of the avoided crossing must be between the adiabatic and diabatic limits in order for there to be an effective competition between CICS and CINL, otherwise just one of the collision-induced processes will be observed. The relative energies of the neutral loss and charge-separation asymptotes determine whether the curve crossing lies at an appropriate internuclear distance to allow the competition between CINL and CICS [19]. Therefore, in this model, the competition between neutral loss reactions and charge separation following dication collisional excitation is a consequence of the energetics of the dication system.

Previous theoretical estimates have shown that the CINL and CICS asymptotes must be separated by $\approx$2–5 eV for the curve crossing to lie between the diabatic and adiabatic limits [14–16]. As shown in fig. 3, the separation of these asymptotes is determined by the difference between the energy required to form the dicationic product of the CINL reaction (XF_{n-1}^{2+}) from the corresponding singly charged ion (XF_{n-1}^{+}) and the first ionization potential of the neutral species lost in the CINL process. For many small dications, the neutral loss and charge-separation asymptotes are separated by significantly more than 5 eV, for example $\approx$11 eV in the case of CO^{2+}. However, the dications like CF_3^{2+} and SF_4^{2+} have two features which combine to bring these two asymptotes closer together. First, F atoms, which are the neutral species involved in each of the examples (eq. (3)), have a high ionization potential. Second, the ionic species observed as products from the neutral loss reactions are triatomics or larger species (e.g. SF_3^{2+}) whose corresponding singly charged species (SF_3^{+}) will have markedly lower ionization potentials than typical diatomics. These energetic factors could, in larger fluorinated dications, bring the curve crossing to favorable locations (fig. 3) where CICS and CINL can compete effectively. Unfortunately, precise estimates of the potential energy curves and the avoided crossing radius cannot be performed

since the energetics of these larger dications are not well determined.

At present, insufficient experimental data are available to distinguish between either of the two general classes of mechanisms outlined above, or to determine if additional mechanisms are operating. The curve crossing model (fig. 3) does provide clear energetic arguments which would make CINL channels significant only for specific larger dications. However, in this picture of the reaction it is not easy to explain the CINL reaction of SF_4^{2+} to give both SF_3^{2+} and SF_2^{2+} with comparable intensities.

In conclusion, we observe substantial neutral loss reactions, resulting in the formation of a stable daughter molecular dication, following collisions of CF_3^{2+}, SF_4^{2+}, SF_3^{2+} and SF_2^{2+} with the rare gases. In contrast to the collisional reactivity observed for the majority of molecular dications, neutral loss reactions appear to be a common decay pathway for triatomic, and larger, fluorinated molecular dications. It is not yet possible to identify a definitive picture regarding the CINL reaction mechanism. Additional detailed experimental studies of the CICS process may provide missing mechanistic information. Theoretical studies of the structure of these polyatomic fluorinated dications and of the dynamics of the neutral loss process would prove extremely valuable.

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Volume 6: Coadsorption, Promoters and Poisons

Although there has been a tremendous development of new techniques to facilitate the study of well-characterised surfaces, there remains a dearth of publications devoted to the application of these methods. This is particularly true in the case of multi-technique studies, directed to understanding key aspects of surface chemistry and physics. This series of books sets out to rectify this state of affairs by providing reviews which concentrate on the scientific achievements in terms of new understanding of the chemical physics of surfaces, rather than the methodology. Since the earlier volumes have appeared, there has been an increasing shift of emphasis to these multi-faceted approaches to understanding surface chemical problems, which makes the series even more appropriate to the needs of the research community.

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The book should be of interest to the many researchers in the field of surface science (coming from backgrounds in chemistry, physics and materials science), as well as to those interested in heterogeneous catalysis.

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